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TECHNICAL REPORT NO. 4

THE ADSORPTION OF H<sub>2</sub> D<sub>2</sub> ON  
FE (100) -KINETICS AND ENERGETICS

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## ABSTRACT

The adsorption behavior of  $H_2$  and  $D_2$  have been studied on an Fe(110) single crystal surface using a combination of thermal energy atom scattering (TEAS) and angle resolved thermal desorption spectroscopy (ARTDS). TEAS has been used to monitor adlayer coverage during adsorption, desorption and at equilibrium over a range of constant temperatures; and during temperature programmed desorption. ARTDS has been used to measure the desorption flux as a function of surface polar angle during temperature programming following adsorption at low temperature.  $H_2$  and  $D_2$  adsorb directly, dissociatively, with an activation energy for adsorption of slightly less than 1 Kcal/mol, and an initial sticking coefficient of about 0.1, independent of temperature. The sticking coefficient decreases with increasing coverage as  $(1 - \theta)^2$ . Desorption kinetics are second-order, with activation energies of 25 Kcal/mol ( $H_2$ ) and 26 Kcal/mol ( $D_2$ ). The isosteric heats of adsorption, for  $\theta \leq 0.5$ , for the two gases are 24 Kcal/mol ( $H_2$ ) and 25 Kcal/mol ( $D_2$ ).

The adsorption and desorption behavior of H<sub>2</sub> and D<sub>2</sub> have been measured on an Fe(110) surface using a combination of thermal energy atom scattering (TEAS) and angle resolved thermal desorption spectroscopy (ARTDS) techniques.

The sample studied was a disc 1.0 cm in diameter and 0.05 cm thick, cut from a sheet that had been recrystallized by strain anneal. The sample was cleaned by cycles of argon ion bombardment and anneal, followed by oxygen titration of residual carbon. Cleanliness of the surface was characterized by the intensity of a specularly scattered helium atom beam, which is much more sensitive to contamination than techniques such as Auger electron spectroscopy.

The change in adlayer coverage with time for an initially clean surface exposed to a constant background pressure of H<sub>2</sub> and D<sub>2</sub> was measured by observing the decrease in the specularly scattered helium intensity due to inelastic scattering by the chemisorbed hydrogen or deuterium atoms. Calibration of the scattered intensity vs coverage data yielded scattering cross sections of  $3.36 \pm 0.17 \text{ \AA}^2$  for deuterium and  $3.47 \pm 0.35 \text{ \AA}^2$  for hydrogen.

Analysis of the transient observed when the clean surface was exposed to H<sub>2</sub> or D<sub>2</sub> showed that the initial sticking coefficient was independent of temperature over the range from 200 to 450 K. Aside from an initial transient, probably associated with a small concentration ( 5%) of surface defects, the sticking coefficient decreased as  $(1-\theta)^2$ , as expected for direct dissociative adsorption following Langmuir-type kinetics.

Analysis of the desorption transient observed when the gas phase H<sub>2</sub> or D<sub>2</sub> pressure was suddenly reduced to a very low value indicated second-order desorption kinetics. Measurements over a range of temperatures led to desorption rate constants of

$$k_d = (2.5 \pm 1.3) \times 10^{-3} \exp (-25100 \pm 1300/RT) \text{ molec/cm}^2 \cdot \text{s}$$

for hydrogen and

$$k_d = (8.1 \pm 2.3) \times 10^{-3} \exp (-26100 \pm 1000/RT) \text{ molec/cm}^2 \cdot \text{s}$$

for deuterium for total coverages below 0.5 monolayers.

The equilibrium adsorbate coverage was also measured over a range of temperatures and pressures, and used to construct adsorption isosteres. Analysis of these curves yielded heats of adsorption of 24.2 ± 2.4 kcal/mol for hydrogen and 24.7 ± 2.9 kcal/mol for deuterium.

The desorption kinetics of hydrogen and deuterium were also measured by using the specular helium peak intensity to monitor adsorbate coverage as the surface was heated, as in a conventional temperature programmed desorption experiment. Analysis of the coverage vs temperature data obtained yielded desorption rate constants of

$$k_d = (3.5 \pm 1.3) \times 10^{-3} \exp (25900 \pm 1400/RT) \text{ molec/cm}^2 \cdot \text{s}$$

for hydrogen and

$$k_d = (5.1 \pm 1.7) \times 10^{-3} \exp (26400 \pm 1200/RT) \text{ molec/cm}^2 \cdot \text{s}$$

for deuterium.

The desorption kinetics of hydrogen and deuterium from this same surface were also measured using angle resolved temperature programmed desorption (ARTPD). In these studies, the sample was first exposed to a predetermined flux of H<sub>2</sub> or D<sub>2</sub>, then heated at a linear rate. Desorbed gas was detected by a quadrupole mass spectrometer, located in a separately pumped chamber, and apertured so as to have an acceptance angle of 2° as seen from the sample.

Measurements made for constant exposures of 522 and 6.5 Langmuir, over a range of angles relative to the substrate normal, indicated an angular dependence of the desorption flux of  $\cos^2.18\theta$ . This indicates the presence of a barrier to adsorption. The magnitude of this barrier was calculated based on both the Van Willigen model, (1) which assumes a one-dimensional barrier parallel to the surface, and the Comsa and David model, (2) which assumes a one-dimensional barrier with "holes". In our calculation, we assumed 5% holes, consistent with the fractional coverage required to reach the  $(1 - \theta)^2$  sticking coefficient dependence measured by TEAS. Results of these calculations gave values of the activation energy for adsorption of 600 cal/mol (Van Willigen) and 700 cal/mol (Comsa and David).

Thermal desorption measurements for desorption normal to the sample surface, after correction for the non-thermal velocity distribution derived from the angle-dependent desorption measurements, were in complete agreement both with the previous results of Boszo et al (3), and with the results of the TEAS measurements described above. The desorption rate constant for deuterium calculated from these results was

$$k_d = (5 \pm 2) \times 10^{-3} \exp(-27300 \pm 1800/RT) \text{ molec/cm}^2 \cdot \text{s.}$$

Due to a high hydrogen background in the detector, no value of the desorption rate constant could be obtained for hydrogen.

Taken together, the two sets of measurements provide a consistent picture of the adsorption-desorption behavior. Adsorption proceeds directly, without the influence of a precursor state, with an activation barrier of roughly one Kcal/mol. Desorption is a second order process with an activation energy of roughly 25 Kcal/mol (hydrogen) and 26 Kcal/mol (deuterium). Note that the measured heats of adsorption are less than the corresponding activation energies for desorption by roughly one kcal/mol, as would be expected for an activation energy for adsorption of this magnitude.

It should be noted that the results described above are in direct contradiction to our previously published results on the same system (4). We now believe the previous results to be spurious, having been strongly influenced by adsorbed impurities arising from regurgitation of previously pumped gases from the system ion pump. This is a potentially serious problem in the use of helium scattering to monitor adsorption, as the technique does not differentiate among adsorbates. Precautions were taken in the present work to avoid this problem.

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